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Multicolor Luminescence Switching, and Controllable Thermally Activated Delayed Fluorescence Turn on/Turn off in Carbazole- Quinoxaline-Carbazole Triads

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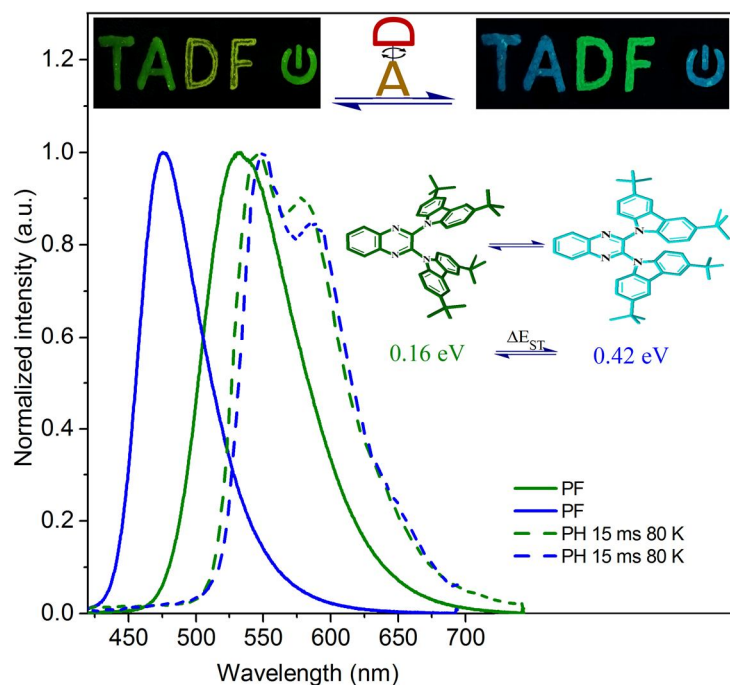
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ABSTRACT: In this work we report a series of thermally activated delayed fluorescence (TADF) molecules with mechanochromic luminescence (MCL) properties and reversible TADF turn on/off properties in solid state that are induced by the transition between amorphous and crystalline states. Additionally, multicolor altering through external stimulus is demonstrated. All the studied compounds exhibited recovery of the initial states associated with narrower emission spectra. TADF OLEDs fabricated by solution processing rendered high external quantum efficiency up to 10.9% and luminance of 16760 cd m⁻².

TOC GRAPHICS



The concept of donor-acceptor-donor (D-A-D) molecular systems has played an important role in the design of materials with MCL properties and organic semiconductor materials for application in optoelectronic devices, such as solar cells, organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), etc.¹⁻³ OLEDs are already entering commercial applications in various areas where screen displays are of interest, such as smart phones and TVs, and their application provide ways to produce thin, flat and flexible panel displays. Nowadays, vacuum thermal deposition is the dominant method for manufacturing OLEDs. However, thermally evaporated OLEDs require large amounts of organic materials to be used and need special conditions to hold high vacuum in spacious evaporation chambers.⁴ In contrast, solution-processed devices have attracted great interest due to the manufacturing low-cost and possibility of large area deposition by either inkjet or roll-to-roll printing, but have still not proven their merits in terms of device efficiencies, where these simpler devices are clearly lagging behind vacuum sublimed OLEDs.^{5,6}

Unfortunately, in OLEDs the electrical current that drives the device generates emissive and non-emissive species in a ratio 1:3. This is due to the formation of triplet species, which are typically non-emissive at room temperature. Therefore, mechanisms to harvest dark triplet states are paramount to maximize device efficiency. TADF molecules, set out based on metal-free emitters, provide access to 100% internal quantum efficiency (IQE) by using the thermal energy to promote the up-conversion of dark-triplet states into emissive singlet states at higher energy. The application of these materials in OLEDs has been introduced by Adachi *et al.* in 2009 as the third-generation of OLED materials, while the second generation involved expensive heavy metals in phosphorescent metalocomplexes.^{7,8} The principle of TADF is built on a molecular design that ensures a small energy gap between the lowest singlet (S_1) and triplet (T_1) states, (ΔE_{ST}), whose sole purpose is to promote efficient up-conversion of triplet excitons into singlet excitons by

reverse intersystem crossing (rISC). Achieving small ΔE_{ST} occurs by minimizing the overlap between the HOMO and LUMO orbitals either by introducing a bridge or a twisted D-A structure.⁹ However, a small overlap between the HOMO and LUMO orbitals also decreases the oscillator strength (f), and so the radiative rate constant (k_r). This leads inevitably to a decrease in the luminescence efficiency.¹⁰ There is, therefore, a particular interest on the design of molecules with a small ΔE_{ST} but still showing strong radiative efficiency.

Mechanochromic luminescent (MCL) materials have also piqued considerable attention recently, due to the possibilities offered to achieve tuning and switching on and off of their luminescence by using external stimuli.^{11,12} Moreover, MCL materials show potential for wide applications in a range of fields including memory devices, sensors and data storage.¹³ In general, the mechanochromic behavior is observed following an external stress, such as grinding, heating, fuming and melting or pressing, and it is induced by either conformational changes that alter dipole-dipole interactions or changes in the intermolecular interaction between adjacent molecules.¹¹ Although numerous MCL materials have been reported in the literature, the development of highly pure photoluminescence (PL) color and multicolor switching materials remain a significant challenge.¹⁴⁻¹⁶ Recently, Swager *et al.*¹⁷ and Takeda *et al.*¹⁸ have reported TADF emitters that also show MCL behavior, however in their studies no thorough analysis of the prompt and delayed emissions was performed in solid state.

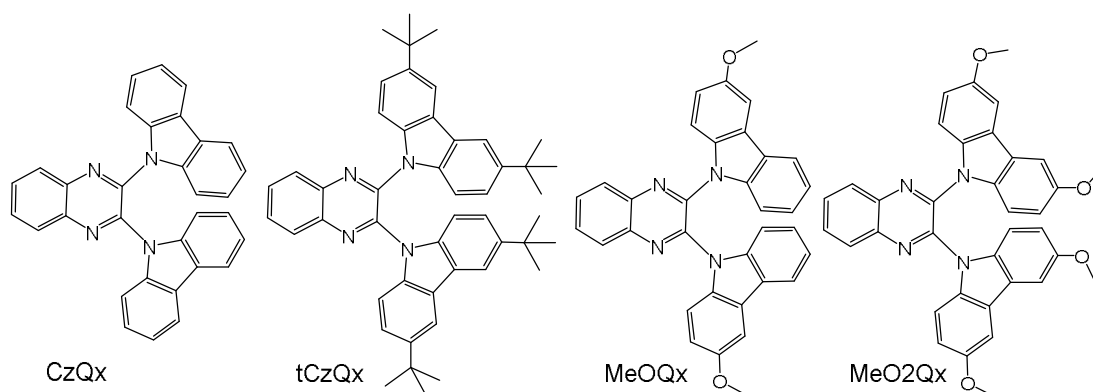


Figure 1. Chemical structures of compounds described in this work

Herein we report the design, synthesis and photophysics of four new multifunctional MCL-TADF luminogens (**Figure 1**), showing strong MCL properties, and study their electroluminescence in OLEDs. A smaller number of synthetic steps, catalyst-free synthesis and high reaction yields are the significant features of the synthetic procedure presented in this study. Moreover, electron-rich donor, 3-methoxy-9*H*-carbazole, is used to investigate the effect of methoxy substitution on the carbazole moiety. All the four emitters behave as multifunctional materials and render MCL behavior, showing multicolor emission in solid state upon external stimulus. Cumulatively, high brightness and external quantum efficiency (EQE) is obtained in solution processed OLEDs. To gain more insight into the mechanism affecting the mechanochromism properties, we probed the TADF characteristics of the four compounds in their different solid forms. Remarkably, tCzQx exhibited reversible TADF turn on/off by applying external forces.

Owing to the valuable properties of carbazole derivatives such as high thermal and chemical stability and low redox potentials, they are used as electron donor units.^{19,20} Synthetic routes towards carbazole-quinoxaline-carbazole derivatives are shown in **Figure S2**. The acceptor moiety was obtained via reaction of *o*-phenylenediamine with oxalic acid, and then reaction with thionyl chloride.²¹ In the next step, the *N*-arylation was performed through nucleophilic aromatic

substitution (S_NAr) process between 2,3-dichloroquinoxaline and carbazole derivatives giving target products in medium to high yields. The structures were confirmed by 1H -NMR, ^{13}C -NMR and mass spectroscopy (details are described in the supporting information).

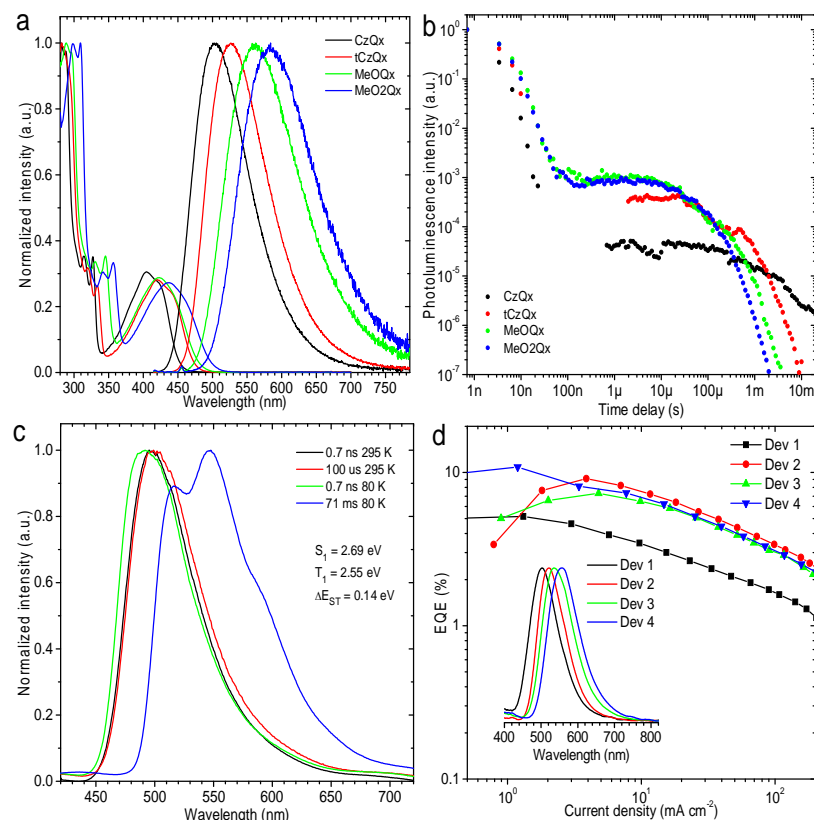


Figure 2. Normalized absorption and fluorescence spectra ($\lambda_{exc} = 400$ nm); b) PL decays of all molecules dispersed in Zeonex 1% (w/w) recorded at room temperature; c) Prompt fluorescence, delayed fluorescence and phosphorescence of tCzQx in Zeonex recorded at different temperatures; d) EQE of fabricated OLEDs plotted as a function of current density, inset shows the electroluminescence spectra.

The photophysical properties of the compounds are depicted in **Figure 2** and **Table 1** (further details are presented in the SI). All presented molecules show TADF properties when doped into

Zeonex solid film, however the shortest DF lifetime and largest DF intensity are observed for MeOQx and MeO2Qx. The delayed fluorescence time constants decrease gradually from CzQx to MeO2Qx, which may indicate an increase on the rISC rate constant. This is directly a consequence of increasing the donor strength in the series of CzQx < tCzQx < MeOQx < MeO2Qx. The presence of TADF is confirmed by the power dependence of the delayed fluorescence intensity, showing a strictly linear dependence in all cases (**Figures S5-S8** in the SI).²² The intensity of the TADF emission is also clearly dependent on temperature, showing delayed fluorescence at RT, and phosphorescence at low temperature as it can be seen in SI.

Table 1. Summary of photophysical properties.

Sample	Abs (nm) ^a	PL (nm) ^b	$\Phi_{\text{PL}}^{\text{deg}} / \Phi_{\text{PL}}^{\text{air c}}$	S_1 / T_1 (eV) ^d	ΔE_{ST} (eV) ^e	$T_g / T_g / T_d^f$	HOMO/LUMO (eV) ^g	E_g (eV) ^h
CzQx	404	503	0.13 / 0.11	2.87 / 2.59	0.28	161/-/320	-5.85/-3.08	2.75
tCzQx	419	527	0.32 / 0.16	2.69 / 2.55	0.14	-/127/346	-5.54/-2.97	2.63
MeOQx	423	560	0.13 / 0.07	2.63 / 2.51	0.12	106/207/342	-5.64/-2.97	2.60
MeO2Qx	437	582	0.13 / 0.07	2.58 / 2.44	0.14	-/110/365	-5.75/-2.90	2.49

^aCT band absorption maxima in toluene solution; ^bemission maxima in toluene solution; ^cphotoluminescence quantum yield in degassed and air-equilibrated toluene solution; ^dsinglet and triplet energy in Zeonex 1% (w/w) film; ^esinglet-triplet energy splitting in Zeonex 1% (w/w) film; ^fDetermined by DSC and TGA measurements; ^gHOMO and LUMO energy determined by cyclic voltammetry in DCM; ^henergy gap in toluene.

Interestingly, in these molecules the energy of the low energy triplet state that clearly is located on the acceptor (T_1),²³ depends on the donor unit (**Figure S5-S10**). This is a visible sign that the D-A units are not fully decoupled, so there is still some conjugation between them, which is important to increase the radiative decay process. The electron-donating effect of the donor, therefore, affects the electron density on the acceptor, thus decreasing the triplet energy. For that reason the ΔE_{ST} is not significantly smaller in MeOQx/MeO2Qx than in tCzQx as along with

decreasing CT energy, the ^3LE energy decreases as well. The same origin of phosphorescence (the lowest energy triplet localized on the acceptor) is confirmed by a similar vibronic pattern of all phosphorescence spectra and by the fact that in all cases the triplet energy of the donor is clearly higher than the one observed in the D-A-D systems. The influence of the donor moiety on the localized triplet state, thereafter identified as the ^3LE state, implies the local triplet state is not entirely local, rather it is partially delocalized. This shows that speaking about ^3LE of a D-A-D system in terms of an isolated acceptor (or donor) triplet state is not always correct. However, as the state is only partially delocalized, the term ^3LE , will still be used for the purpose of this work. To further prove our statement we recorded the phosphorescence spectra of some of the donors, as the triplet energy of carbazole and di(*tert*-butyl)carbazole is already reported in the literature.²⁴⁻²⁶ In all cases the triplets of the individual donor molecules appear at much higher energy than the ^3LE states in our D-A-D molecules. Moreover, the spectra do not completely match each other (see SI **Figure S9 and S10**).

It is also interesting to note that all TADF emitters in this group show clearly biexponential decay in the DF region whereas the phosphorescence is in all cases strictly monoexponential. This indicates that the effect on the DF decay originates from the CT state rather than appearing as a result of inhomogeneity of the sample. The observation of complex decays in the DF region is thus probably due to the emitter adopting several different (possibly meta-stable) geometries in the excited state, therefore, more than one CT state energy is present, and this renders slightly different rISC rates, as there are different S-T energy gaps. These geometries most likely differ in the dihedral angles between donor and acceptor, which affect the CT but not the more localized triplet state. It is also worth to note that the longest phosphorescence lifetime is observed for tCzQx and the shortest one for MeO2Qx (see SI for details).

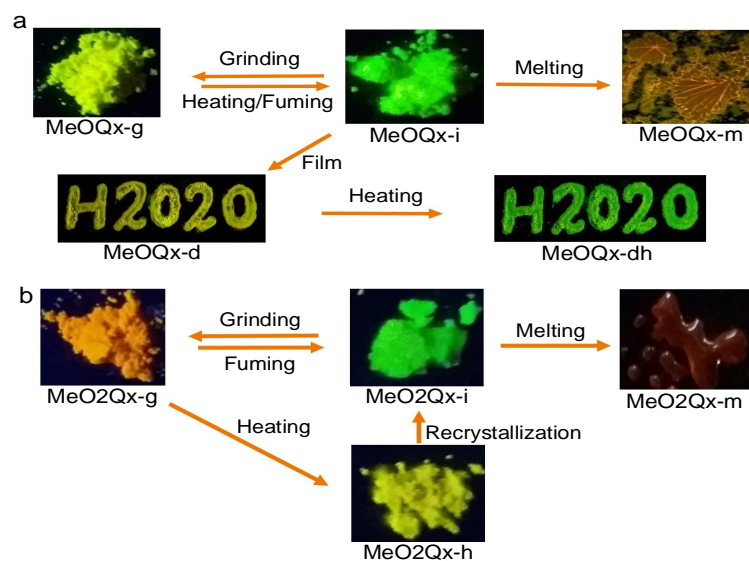


Figure 3. Photographs of the photoluminescence of various forms of (a) MeOQx and (b) MeO2Qx in response to various external stimuli (The photographs taken under excitation wavelength of 365 nm)

Several organic MCL compounds based on cyano-distyrylbenzene scaffold were synthesized in the past.^{1,27} In this context, we introduce here a new strategy for the design of MCL and TADF compounds. The photophysical properties of the four compounds studied here in their solid forms show alterations that are induced by external stimuli and exhibited MCL behavior. Remarkably, MeOQx and MeO2Qx show multicolor alteration in response to external forces (see **Figure 3**). Measurements of the TADF emission were used as a complementary approach to clarify our understanding of the microstructure and phase transformation of the compounds, alongside powder XRD analysis, (details are depicted in the SI). The crystalline structures of the initial powders were disrupted upon grinding with a spatula, creating the amorphous state. On the contrary, either upon heating or fuming of previously ground powders clear diffraction peaks arised, manifesting that the initially ground solids reassembled into new crystalline lattices. In contrast, the films obtained by melting and dropcasting were amorphous, except that of CzQx-m. The narrower PL spectra

obtained from the crystalline samples, in comparison with the amorphous ones, indicate a more local character of the emissive CT state (so-called weak CT or hybrid local and CT state: HLCT). Moreover, melting causes a significant luminescence bathochromic shift.

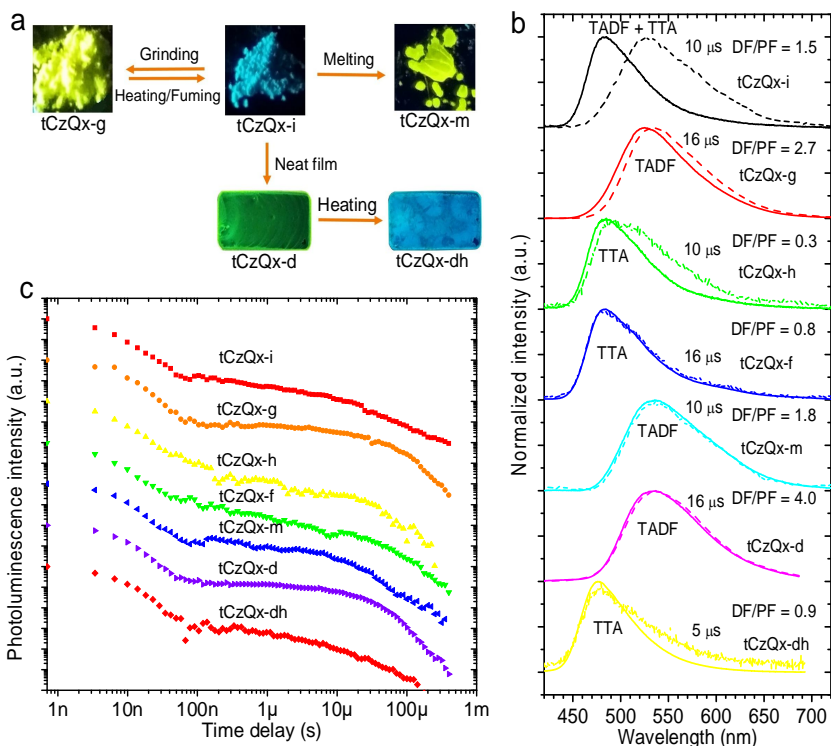


Figure 4. (a) photographs of tCzQx states (b) time-resolved PL spectra and (c) PL decays of different forms of tCzQx. Note the delayed fluorescence spectrum (b) is recorded at the delay stated next to the spectrum, solid and dashed lines denotes prompt and delayed fluorescence, respectively.

For example, in the prepared form, tCzQx-i presents sky blue emission, which upon grinding to form tCzQx-g, shifts towards yellow emission. Heating (tCzQx-h) and fuming (tCzQx-f) of tCzQx-g powder reproduces powder of sky-blue fluorescence. Remarkably, PL of tCzQx-i, tCzQx-h, and tCzQx-f, is blue-shifted relative to the emission of the solution in hexane. This suggests that the emissive singlet state has more localized character than the emissive state in a

non-polar solvent, i.e. the intermolecular interactions present in the solid forms are less effective on relaxing the molecular structure than in the liquid solution. The red shift of the photoluminescence after grinding (tCzQx-g) also implies a transformation of the excited state from the LE (or HLCT) state into an intramolecular charge transfer (ICT) state, which indicates a relaxation of the D-A dihedral angle. This is consistent with less predominant intermolecular interactions in the amorphous than in the crystalline form, and probably more free space to allow the molecules to adapt their conformation in order to stabilize the charge transfer state. Finally, annealing of the amorphous drop casted film of tCzQx (tCzQx-d) results in formation of a crystalline state (tCzQx-dh) which recovers sky blue emission (**Figure 4**). Further, the time-resolved photoluminescence studies of prompt and delayed emissions from different forms were also performed. Notably, the amorphous forms of tCzQx demonstrated strong TADF, whereas, in the crystalline phase very little or no delayed fluorescence was observed. This surprising behavior implies that introducing of heavy substituents (t-Bu) rigidified donor around C-N bond, thus descending vibrational rotation and non-radiative decays. In the crystalline form the weak delayed fluorescence appears mostly as the result of triplet-triplet annihilation (see SI for details). This phenomenon is exceptionally important, because represents that molecular assembly and external stimuli, along with molecular design and host effects²⁸ are parameters that can control the formation of the CT state, influence the TADF behavior.

Briefly, as the amorphous phase is expected to be less dense, and so carrying more free space, the donor and acceptor moieties can more freely rotate around C-N bond. This results in a relaxed charge transfer conformation, probably with larger donor-acceptor dihedral angle. Therefore, PL spectrum red-shifts after transformation from crystal to amorphous form, consistently with the larger stabilization of the CT state. In the crystal form the larger intermolecular interactions that

are prevalent in the ordered packing reduces the free space and probably forces spacious donor/acceptor units to adapt a relatively less twisted configuration. This decreases the donor-acceptor dihedral angle, and consequently leads to weakening of the CT character, which in fact becomes of more of localized nature (such as a hybrid local and CT state). As in both forms the local triplet state (^3LE) is practically not affected by the D-A dihedral angle (due to the localized nature), the change induced on the energy of the singlet CT state can either promote TADF (amorphous phase) or quench it (crystal phase) due to a change in ΔE_{ST} . This is evidenced in **Figure S19** where prompt fluorescence and phosphorescence of drop casted films is presented. Clearly, in tCzQx-d and tCzQx-dh forms the phosphorescence not only resembles that observed in Zeonex, but also remains nearly identical in either case. Changes are only observed on the CT energy, which is evidence that the observed alternations are driven entirely by the change in D-A dihedral angle. The similar behavior is observed for powders, and therefore, can be explained by the same mechanism. Interestingly, tCzQx in powder form gives not only a switchable color of luminescence, but also reversible turn-on / turn-off TADF luminescence (**Figure 4**).

For the CzQx powders the results demonstrate the coexistence of amorphous and crystalline forms, showing green and blue emissions. Introducing stronger donors in the case of MeOQx and MeO2Qx resulted in a high contrast emission change from green to red. The annealed form of MeO2Qx-h, showed yellow emission and the fumed form of MeO2Qx-f resembled the emission of the initial form (**Figure3**). Accordingly, the X-ray diffractogram of MeO2Qx-h shows significantly different patterns compared to those of other crystalline samples, e.g. MeO2Qx-f (**Figure S28**). This suggests that MeO2Qx can have distinct crystal structures with different D-A dihedral angles. It is particularly interesting that the heated form shows a relatively narrow emission band, compared to those of MeO2Qx-i and MeO2Qx-f, suggesting a more rigid structure.

In order to show the versatility of the presented molecules their triplet harvesting properties are highlighted by their performance in OLEDs. Due to the very good solubility of the compounds in toluene and good TADF properties of the films, the devices were fabricated by solution processing.

Table 2. Summary of device characteristics.

Device	Turn on at 5 cd m ⁻² , V	EQE (%) / Current efficiency (cd A ⁻¹)			Max. cd m ⁻²	CIE (x,y) at max. brightness
		max.	at 100 cd m ⁻²	at 1000 cd m ⁻²		
Dev 1	5.9	5.4 / 14.2	5.0 / 13.1	3.3 / 8.5	5397	0.22, 0.40
Dev 2	5.0	9.1 / 28.9	3.2 / 12.8	8.8 / 28.3	15290	0.29, 0.55
Dev 3	5.0	7.3 / 22.7	5.0 / 11.2	7.2 / 21.8	12910	0.36, 0.55
Dev 4	5.0	10.9 / 27.2	9.6 / 24.5	7.9 / 24.2	16760	0.41, 0.53

Device structure: ITO | HIL 1.3N (45 nm) | PVKH (10 nm) | PVK:PBD (60:40) co dopant 5% (32 nm) | TPBi (50 nm) | LiF (0.8 nm) | Al (100 nm). Where PVK denotes poly(*N*-vinylcarbazole) with average molecular weight of 90 000 g mol⁻¹ while PVKH denotes poly(*N*-vinylcarbazole) with 1.1 • 10⁶ g mol⁻¹ average molecular weight. Dopants: Dev 1=CzQx, Dev 2=tCzQx, Dev 3= MeOQx, Dev 4= MeO2Qx

All four compounds give efficient green-blue to green-yellow OLEDs. High-molecular-weight poly(9-vinylcarbazole) (PVKH) was used for electron-blocking and hole-transporting layer to improve charge confinement in the emitting layer. Since PVKH does not dissolve in toluene at room temperature, PVK:PBD blend was used as a host due to its superior film-forming and well-balanced charge-transporting properties. The devices showed electroluminescence changing from blue-green (Dev 1) to yellow-green (Dev 4). Overall the devices show excellent EQE over 5 % and up to 10.9 %, giving clear indication that triplet excitons are being harvested by the TADF mechanism. The best EQE is observed for Dev 4 which contains MeO2Qx as dopant. Devices 2-4 are similar to each other, but Dev 1 is much less efficient and shows higher turn-on voltage. The lower efficiency of Dev 1 is explained by the lower contribution and longer lifetime of the TADF

luminescence (see SI), while the higher turn-on voltage is a consequence of the highest HOMO energy of CzQx, among all studied molecules.

In summary, new donor-acceptor-donor compounds are presented as highly luminescent TADF emitters with remarkable mechanoluminescent properties under external stimuli. The compounds not only exhibit TADF properties at low (1-5%) concentrations, as doped in Zeonex or PVK:PBD matrix, but also in condensed state as neat films and powders. Their good solubility in toluene allows production of efficient and bright solution-processed OLEDs with EQE up to 10.9 %. Photophysical and X-ray diffraction investigations of neat films and powders reveal that the crystalline states show a blue-shifted emission relative to the amorphous forms, which is consistent with the higher PLQY observed for the crystalline forms. Most of the forms show TADF emission which is facilitated by suppression of triplet-triplet annihilation and non-radiative decay processes in the solid state. The tCzQx material shows a perfect TADF behavior in amorphous film (tCzQx-d), while upon crystallization (tCzQx-dh) the TADF is quenched (and TTA is present). This is associated with larger S-T gap in crystalline form relative to the amorphous form due to the increase of the singlet CT energy. In general, stronger donors determined shorter TADF lifetime, higher emission contrast and multi-color luminescence switching. The materials show not only emission color change, but also reversible turn on/off of TADF properties under external stimuli.

ASSOCIATED CONTENT

Supporting Information

Details of synthetic procedures, photophysical, thermal, electrochemical properties, PXRD data, and device characteristics (PDF).

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Notes

The authors declare no competing financial interests.

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